

UDC 666.295.4:546.82.001.5

FORMATION OF A GLAZE COATING STRUCTURE BASED ON LOW-BORON ZIRCONIUM-CONTAINING GLASS

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Translated from *Steklo i Keramika*, No. 1, pp. 19–22, January, 1999.

The structure of initial glasses with 7.5–15.0 mol.% of B_2O_3 and glaze coatings based on these glasses is investigated. The initial glasses exhibited a liquation structure. It is established that the primary crystal phase released in heat treatment is anorthite and not the zirconium-containing phase as was observed in glazes with a higher content of B_2O_3 . The crystal phases are formed on the basis of liquation drops.

The development of glaze compositions with a decreased content of boron anhydride is an important goal, due to the high cost of boron-containing materials. However, boron anhydride is a necessary component of glaze glasses. It is a unique flux which ensures a low melting point together with a significant decrease in the thermal coefficient of linear expansion (TCLE).

The glaze coatings for building ceramics are formed at a temperature of 850–950°C, therefore, the initial glass should be sufficiently low-melting to ensure good spreading at the firing temperatures. However, in addition to a low melting point, strict TCLE requirements are imposed upon the formed coatings, in order to provide for consistent seal between the glaze coating and the ceramic base. However, the TCLE of the glaze coating is determined not only by the TCLE of the initial glass, but also by its phase composition and structure evolved in heat treatment. Therefore, it is interesting to study the specifics of structure formation in glaze coatings based on low-boron glass.

We studied the synthesis of opacified zirconium-containing glazes with a B_2O_3 content within the limits of 7.5–15.0% (here and elsewhere, the molar concentration is given unless otherwise specified) based on the Na_2O – CaO – B_2O_3 – Al_2O_3 – ZrO_2 – SiO_2 system. The amount of other oxides was (%): 50–60 SiO_2 , 10–15 Al_2O_3 , 215–25 (Na_2O + CaO), 4 ZrO_2 . The glass was made in porcelain crucibles of 0.3 liter capacity in a gas-flame furnace at the temperatures of 1350–1400°C with holding at the maximum temperature for 1–1.5 h. The glass exhibited good melting and working properties. Virtually all glasses retained their clarity in frit granulation.

Since the structural state of the boron in the glass significantly affects spreading and the properties of glazes, we performed an IR-spectroscopic analysis of the experimental glasses and glasses heat-treated within the temperature inter-

val of 750–1050°C. The mutual effect of the aluminum and boron ions on their structural state in aluminoboron-silicate systems was taken into account as well [1, 2].

Figure 1 shows the IR absorption spectra of glasses with a different content of Al_2O_3 and B_2O_3 , whereas the sum of the alkali and alkaline-earth oxides was relatively constant

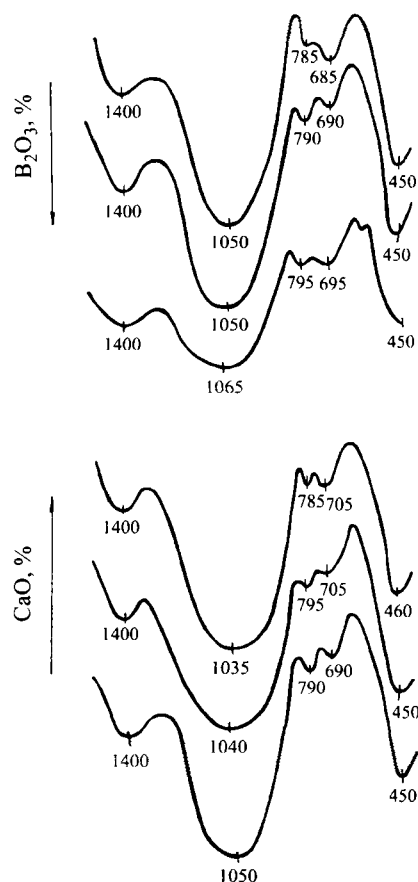


Fig. 1. Infrared spectra of initial glasses with a different content of B_2O_3 and CaO .

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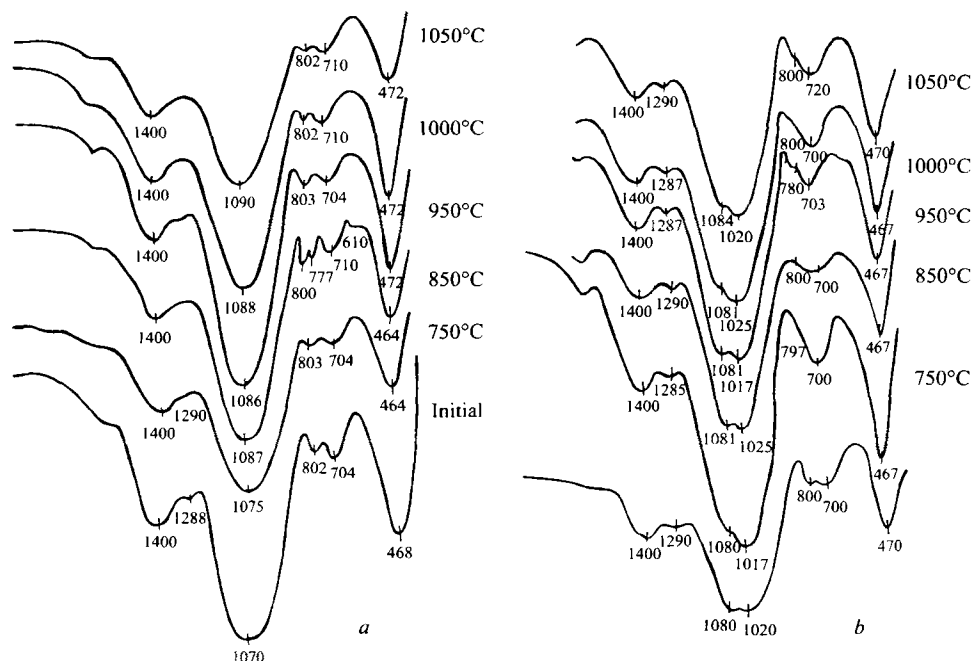


Fig. 2. Infrared spectra of heat-treated glasses: a) glass 1 containing 15% B_2O_3 ; b) glass 2 containing 7.5% B_2O_3 .

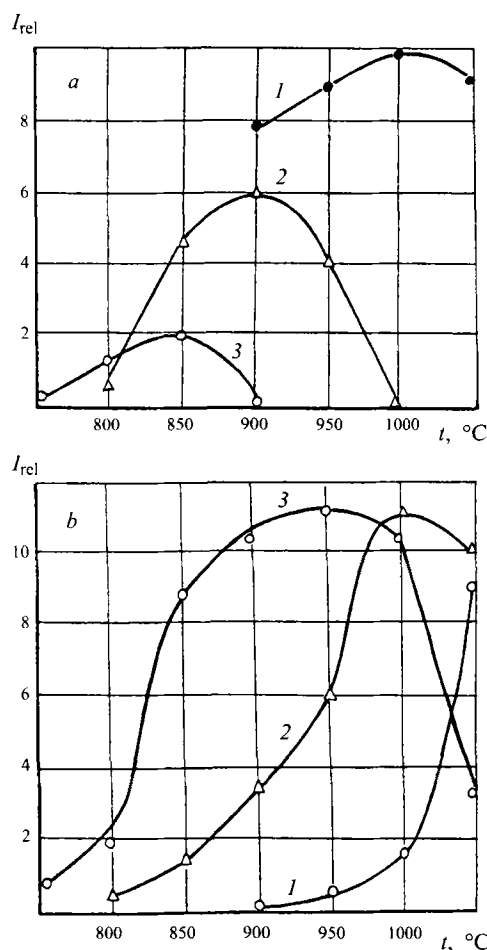


Fig. 3. Relative change in the content of the crystal phases in heat treatment of the glaze coating of compositions 1 (a) and 2 (b): 1) zirconium; 2) rufite; 3) anorthite.

(21%). The spectra were recorded using a Specord IR-75 infrared spectrophotometer on pelleted glass powders with KBr in the ratio of 1 : 300.

The initial glass spectra exhibit absorption bands in the regions of 1400, 1050 – 1065, 720 – 700, 690, and 450 cm^{-1} . The main absorption band (1050 – 1065 cm^{-1}) corresponds to vibrations of Si – O – Si asymmetric bonds in relatively highly polymerized groups consisting of $[SiO_4]$ tetrahedrons, which occupy an intermediate position between stratified and skeleton structures. This high degree of polymerization of the silicon-oxygen groups with a SiO_2 content in glazes equal to about 50 – 60% is possible only in the case of additional incorporation of $[AlO_4]$ and $[BO_4]$ groups in the oxygen lattice. The presence of $[AlO_4]$ groups is confirmed by the absorption band at 700 – 720 cm^{-1} . It is obvious that virtually all aluminum ions in the experimental glasses are in four coordination.

The analysis of the possible coordination of boron ions, according to A. A. Appen's data [1] leads to the conclusion that for a $((R_2O + RO) - Al_2O_3)/B_2O_3$ coefficient value in the experimental glasses ranging from 1 to 0.5, the boron ions should be in two coordination states: $[BO_3]$ and $[BO_4]$. The presence of an absorption band in the region of 1400 cm^{-1} confirms the existence of $[BO_3]$ groups. The latter should contribute to an increase in glaze fusibility and spreadability. The presence of $[BO_4]$ groups is apparently minor, since the intensity of the 1400 cm^{-1} band for $[BO_3]$ is substantial. However, the presence of $[BO_4]$ groups in the experimental glasses is rather clearly shown by the electron paramagnetic resonance data. As to the absorption band within the range of 780 – 800 cm^{-1} , it can be assumed to relate to the Si – O bonds as a second component of the sym-

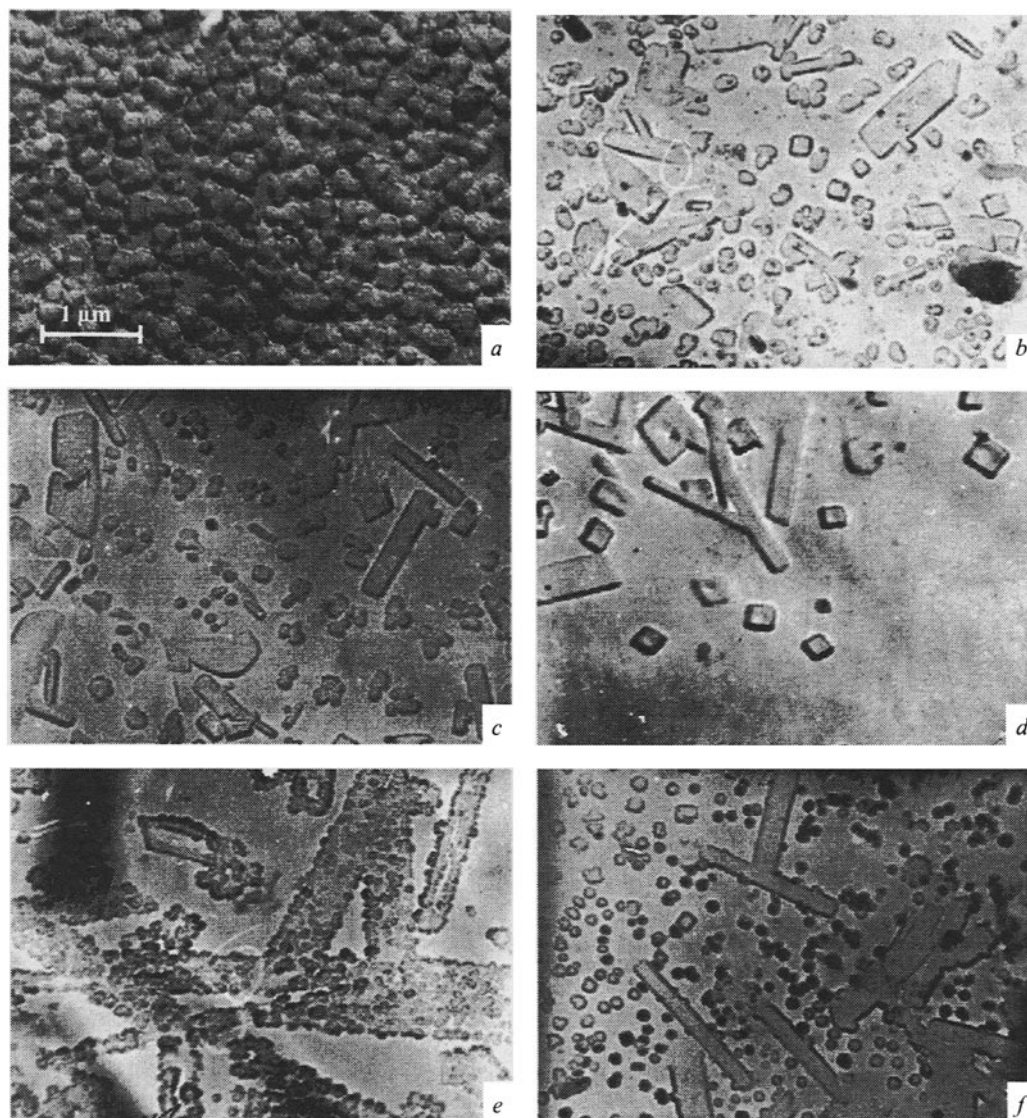


Fig. 4. Electron microscopic studies of the structure of glaze coatings: *a, b, c, d, and e*) glaze of composition 1 (initial glass and coatings heat-treated at 850, 950, 1000, and 1050°C, respectively); *f*) glaze of composition 2 heat-treated at 950°C.

metric stretching vibrations. It is present, for example, in the infrared spectra of such silicates as wollastonite CaSiO_3 (680 cm^{-1}) and barium disilicate BaSi_2O_5 (700 cm^{-1}) [3].

With an increase in the content of B_2O_3 from 10 to 14%, no perceptible changes are observed in the nature of the spectra. With an increase in the CaO content from 6 to 20%, processes of depolymerization of the structural lattice ($1050 - 1030\text{ cm}^{-1}$) and the decrease in the amount of the $[\text{BO}_3]$ groups (decrease in absorption at 1400 cm^{-1}) are quite noticeable, apparently due to an increase in the content of $[\text{BO}_4]$ groups.

A certain increase in the degree of polymerization of the basic structural groups (Fig. 2*a*) is observed in heat-treatment of glass 1 which contains 15% B_2O_3 and 21%

($\text{R}_2\text{O} + \text{RO}$). The maximum of the basic absorption band is shifted from 1070 to 1090 cm^{-1} as the heat treatment temperature increases. Since virtually all aluminum ions in glasses are in four coordination, an increase in the degree of polymerization of the basic structural groups can occur at the expense of conversion of part of the three-coordinated boron to four-coordinated. Indeed, a decrease in absorption is observed in the region of 1400 cm^{-1} relating to $[\text{BO}_3]$ groups. However, both coordinations of the boron ions (three and four) are preserved in this case. Liquation phenomena in the solid glass are weakly manifested, if they happen at all in heat treatment, since no splitting of the basic absorption band is recorded.

As for glass 2 with 7.5% B_2O_3 and 21% ($\text{R}_2\text{O} + \text{RO}$), the liquation processes are clearly manifested in the initial glass:

the basic absorption maximum is clearly seen to be split into two bands, corresponding to high-silica (1080 cm^{-1}) and low-silica (1020 cm^{-1}) phases (Fig. 2b). In this case both phases after heat treatment retain their individual specifics.

Based on the experimental glasses, glaze suspensions were prepared with addition of 5% refractory clay, and tile coatings were produced by heat treatment at firing temperatures from 700 to 1100°C with holding at the maximum temperature for 20 min.

The samples heat-treated within the temperature interval up to 750°C exhibited insufficient spreading, and at higher temperatures the resulting coatings had a great degree of opacity with lustrous and semi-matte texture. At the temperature of $700 - 750^{\circ}\text{C}$, the liquation processes in the glazes intensified, which was caused by the formation of low-silica calcium-borate drop component with predominantly three-coordinated boron, on one hand, and an aluminosilicate highly polymerized matrix component which also included sodium cations, since all these cations had to be localized in $[\text{AlO}_4]$ tetrahedrons, on the other hand.

Similar liquid-phase separation was also registered in glazes of this system which are richer in the B_2O_3 content (up to 30 wt.%) and have a very low Al_2O_3 content (1.7 wt.%), in which one phase is sodium-calcium-borate enriched with zirconium, and the other phase is enriched with silicon [4 - 6]. According to the local x-ray spectroscopic analysis performed on a Comebax unit with a microprobe, it was established that the ZrO_2 in the experimental glazes is mostly concentrated in the calcium-borate component. This is confirmed by the fact that the Zr-containing crystals are formed based on the drop phase.

According to the x-ray phase analysis data of glaze coatings of compositions 1 and 2 (Fig. 3), the first crystal phase is formed at the temperature of 750°C , although it is not a zirconium-containing phase but anorthite. This is a peculiarity of the considered glazes. The first among the zirconium-containing phases is ruffite, i.e., the tetragonal ZrO_2 . Its quantity rapidly increases as the heat treatment temperature increases from 800 to $900 - 950^{\circ}\text{C}$. With emergence of ZrSiO_4 zircon, the content of ruffite in the glaze coating starts to decrease sharply, i.e. it is quite obvious that ZrSiO_4 is formed due to a reaction between the ruffite and the silica from the residual vitreous phase.

The electron microscopic study of the glaze coating structure based on composition 1 and heat-treated at different temperatures indicated that the crystal phase is formed based on liquation drops (Fig. 4a). With emergence of the crystal phase at the temperature of 850°C (Fig. 4b), the liquation drops virtually disappear. The flat crystals of anorthite and the cross-shaped bipyramids of ruffite are clearly visible. With an increase in the heat treatment temperature (Fig. 4c, d), the disappearance of anorthite and the emergence of prismatic crystals of zircon are registered. At a heat treatment temperature of 1050°C , fusion of isolated crystals begins (Fig. 4e). However, in the glaze based on glass 2, liquation processes persist in crystallization as well, which is

clearly seen in the electron microscopic studies of the glaze coatings (Fig. 4f).

In [6 - 8] the authors came to the conclusion that the mechanism of formation of low-melting boron-zirconium glazes consists of at least three stages: phase separation of glass (liquation), formation of ruffite, and synthesis of zircon. The glazes investigated by us have a liquation structure which is already more or less clearly expressed in the synthesis stage. Therefore, further heat treatment only brings about the second stage of phase separation, i.e., crystallization. In this case, liquation can completely disappear or partially persist. Moreover, in the early stage of crystallization, anorthite is actively released. The release of the calcium-containing phases in boron-free zirconium compositions is established in [9]. Apparently, it is regular for low-boron and boron-free glaze glasses.

Thus, low-boron glazes exhibit certain features in the formation of the coating structure which differ from the glazes with a higher content of B_2O_3 . The primary crystalline phase in these glazes is anorthite and not a zirconium-containing phase. The liquation processes are manifested in the stage of synthesis of the initial glass. These processes usually disappear during crystallization.

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